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(54) NONAQUEOUS SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To bring out a capacity exceeding a theoretical capacity of graphite and causing alkaline metal ions or alkaline metal atoms to be stored and discharged with high efficiency over a long time, by sticking metallic particles having a specific grain size, capable of electrochemically storing and discharging alkaline metal ions or alkaline metal atoms on a current collector by means of a binding material.

SOLUTION: Preferably, the average grain size of metallic particles used falls within the range of 1 to 1,000 nm, more preferably, within the range of 10 to 500 nm, and most preferably, within the range of 30 to 400 nm. Preferably, the grain size distribution also falls within these ranges. Preferable metallic particles are alloy particles made up of metals of two or more kinds selected from among a group comprising Sn, Sb, Ag, Cu, and Au, and Sn particles. A binding material used for a negative electrode is used for sticking the metallic particles on a current collector and selected from among materials stable relative to a solvent used at electrode forming and relative to a solvent for an electrolyte.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to nonaqueous rechargeable batteries suitable as a power supply of a small and lightweight electrical machinery and apparatus or an electric vehicle including a lithium secondary battery.

[0002]

[Description of the Prior Art] To enlarge capacity of a rechargeable battery much more and to attain small lightweight-ization of a cell with the miniaturization of electronic equipment in recent years, is desired. For this reason, the nickel cadmium battery and the lithium secondary battery with energy density higher than a nickel hydride battery attract attention. The lithium secondary battery is actually used for portable electronic communication equipment, such as a small video camera, a notebook computer, and a cellular phone, etc. Although to use a lithium metal as a negative-electrode material of a lithium secondary battery at the beginning was tried, while repeating charge and discharge, the dendrite-like lithium which deposits in a negative electrode penetrated the separator, and reached even the positive electrode, and it became clear that there was a danger of causing the ignition accident by the short circuit.

[0003] In order to cope with the problem on such safety, using a graphite with high degree of crystallinity as an electrode is proposed (JP,57-208079,A). If this electrode is used, since a lithium ion will be reversibly made as for occlusion and emitting (an intercalation / day intercalation) to a graphite crystal in the case of charge and discharge, a sludge is not formed on an electrode. However, LiC₆ which is the maximum lithium installation compound even if it uses a graphite as an electrode It is theoretically impossible to obtain the capacity more than geometric capacity (372 mAh/g) under ordinary temperature and ordinary pressure. Since a graphite material, not to mention it, has the low wettability to the electrolytic solution, the lithium dedope capacity in early stages of charge and discharge also has a problem when [actual] saying that 350 mAh/g is not reached, either.

[0004] Then, using the metals (aluminum, Si, etc.) in which alloying with a lithium is possible is proposed as a negative-electrode material which can discover high capacity. However, a remarkable volume change arises by the occlusion of a lithium and emission accompanying charge and discharge, the contact resistance between metal particles increases, and the material proposed until now has the problem that powder-like metal particles separate and fall from a charge collector. For this reason, the fall of the capacity by repeating charge and discharge was remarkable, and there was a problem in considering as the material for rechargeable batteries as a matter of fact. In order to solve the problem of such a capacity fall, the metal used as a charge collector is inserted into the aqueous solution of a metal salt, and using as the negative electrode of a lithium secondary battery the electrode produced by carrying out electrocrystallization of the metal particles which serve as an active material by electrolytic reduction on a current collection body surface is proposed. However, this electrode has the problem that it is difficult to produce in large quantities, and it lacks in industrial practicality.

[0005]

[Problem(s) to be Solved by the Invention] This invention made it the technical problem to solve the trouble of such conventional technology. That is, when charge and discharge were performed, this invention could discover high capacity rather than the conventional graphite system electrode material, and made it the technical problem which should be solved to offer a nonaqueous rechargeable battery smaller than the case where reduction of the capacity accompanying charge and discharge uses a conventional metal or the conventional charge of an alloy. Moreover, this invention was made into the technical problem which offering the nonaqueous rechargeable battery which can be manufactured by the simple method suitable for industrial production should also solve.

[0006]

[Means for Solving the Problem] this invention persons came to complete a header and this invention for having a property which was excellent while a nonaqueous rechargeable battery which uses as a negative electrode an electrode which makes metal particles with a mean particle diameter of 1 micrometer or less come to adhere by binding material on a charge collector showed an expected effect, as a result of inquiring wholeheartedly for said technical-problem solution. That is, this invention offers a nonaqueous rechargeable battery which uses as a negative electrode an electrode which makes occlusion and metal particles with a mean particle diameter of 1 micrometer or less which can be emitted come for alkali-metal ion or an alkali-metal atom to adhere by binding material on a charge collector electrochemically.

[0007] It is desirable to use metal particles more than a kind chosen as an electrode used as a negative electrode from a group which consists of aluminum, Si, Sn, Pb, As, Sb, Bi, Zn, Cd, Ag, Au, Pt, Pd, Mg, Na, and K as metal particles, or an alloy particle which consists of two or more sorts of metals chosen from the group. It is desirable especially to use a metal formed by adding a reducing agent in a solution of a metal salt in this invention.

[0008]

[A gestalt of implementation of a technical problem] An operation gestalt of a nonaqueous rechargeable battery of this invention is explained below at details. A nonaqueous rechargeable battery of this invention is characterized by using a negative electrode which makes metal particles with a mean particle diameter of 1 micrometer or less come to adhere by binding material on a charge collector on a configuration. When metal particles used by this invention are made to adhere on a charge collector by binding material, as long as it is occlusion and the thing which can be emitted electrochemically, especially the class is not restricted in alkali-metal ion or an alkali-metal atom. this specification -- setting -- " alkali-metal ion or an alkali-metal atom -- electrochemical -- occlusion -- and it can emit -- " -- when it is used as an electrode of a cell, it says that alkali-metal ion or an alkali-metal atom can be taken in and out of an electrode reversibly.

That is, it says that an intercalation and a day intercalation can be performed reversibly.

[0009] As a metal which can be used for a negative electrode, aluminum, Si, Sn, Pb, As, Sb, Bi, Zn, Cd, Ag, Au, Pt, Pd, Mg, Na, K, etc. can specifically be illustrated. Moreover, an alloy which uses these metals as a configuration element can also be used. An alloy particle and Sn particle which consist of a metal beyond a NI kind chosen from a group which consists of Sn, Sb, Ag, Cu, and Au as desirable metal particles can be mentioned. Although it is desirable as an alloy particle to use a Sn-Sb alloy, a Sn-Ag alloy, a Cu-Sb alloy, and an Au-Sb alloy, alloys other than these can also be used suitably. In addition, an intermetallic compound is also contained in an "alloy" as used in this specification.

[0010] Metal particles used for a negative electrode may consist of a kind of metals, and may be the mixture of a metal beyond a NI kind. However, mean particle diameter of metal particles used by this invention must be 1 micrometer or less. If mean particle diameter uses metal particles exceeding 1 micrometer, capacity deterioration by repeating a charge-and-discharge cycle will become large, and usefulness as an electrode will be spoiled. It is desirable that it is within the limits of 1-1000nm, as for mean particle diameter of metal particles to be used, it is more desirable that it is within the limits which is 10-500nm, and it is most desirable that it is within the limits which is 30-400nm. Moreover, what particle size distribution also has within the limits of these is desirable.

[0011] Especially a manufacture method of metal particles used for a negative electrode is not restricted. Most desirable manufacture method is the below-mentioned method of making form a metal and grinding this to a moderate particle size by adding a reducing agent in a solution of a metal salt. If this manufacture method is used, a lot of metal particles are producible simple, and if metal particles moreover produced by this manufacture method are used, an electrode which has a more desirable property can be manufactured.

[0012] As a metal salt used for this manufacture method, oxysalts of a Vla element, such as a halogenide of a metal which constitutes the above-mentioned metal particles, a metal carbonate, a nitrate, a sulfate, an iodate, a pyrophosphate, phosphate, a hydroxide, a vanadate, and a chromate, etc. can be used. These may be compound metal salts which consist of a metal beyond a NI kind. A metal salt to be used may be a kind or may be the mixture beyond a NI kind. Although a reducing agent used for this manufacture method will not be restricted especially if it has an operation which returns a metal salt to a metal, it is desirable to use a reducing agent more than a kind chosen from a sodium borohydride, a lithium aluminum hydride, and sodium dithionite.

[0013] A reduction reaction is performed a room temperature bath and by mixing and stirring a metal salt and a reducing agent in an ice bath more preferably. As for reaction temperature, it is more desirable to usually set up within the limits of 1-20 degrees C, and to set up within the limits of 2-5 degrees C. After passing through purification, desiccation, a crack, or washing by acid or alkali solution under an inert gas ambient atmosphere after a reaction, metal particles can be obtained by drying. As an acid for washing, a hydrochloric acid, a nitric acid, a sulfuric acid, an acetic acid, a trichloroacetic acid, etc. can be used. Moreover, an aqueous solution of an alkali hydroxide can be used as an alkali solution for washing.

[0014] After stirring chlorination tin and an antimony chloride in a sodium-citrate solution, adding a sodium borohydride as a reducing agent and specifically depositing an alloy particle in an ice bath, under nitrogen gas, after filtration and rinsing, a hydrochloric acid washes further and a metal-powder object is acquired by drying under an argon ambient atmosphere. As for this metal-powder object, it is desirable to grind to condense and to understand condensation in that case etc. As for these metal particles used for a negative electrode, it is desirable that it is in within the limits whose mean particle diameter is 20-700nm, and it is more desirable that it is in within the limits which is 50-400nm.

[0015] On the other hand, binding material used for a negative electrode is used in order to make metal particles adhere on a charge collector, and it is chosen from stable materials to a solvent used at the time of electrode formation, or a solvent of the electrolytic solution. As binding material, specifically Polyethylene, polypropylene, polyethylene terephthalate, Resin system macromolecules, such as aromatic polyamide and a cellulose; Styrene-butadiene rubber, Rubber-like macromolecules, such as polyisoprene rubber, butadiene rubber, and ethylene-propylene rubber; A styrene butadiene styrene block copolymer and its hydrogenation object, styrene ethylene butadiene styrene block copolymer and its hydrogenation object; -- thermoplastic-elastomer-like macromolecules [, such as a styrene isoprene styrene block copolymer and its hydrogenation object,]; -- syndiotactic 1 and 2-polybutadiene -- Elasticity resin-like macromolecules, such as an ethylene-vinylacetate copolymer, and a propylene, an alpha olefin (carbon numbers 2-12) copolymer; fluorine system macromolecules, such as polyvinylidene fluoride, polytetrafluoroethylene, and a polytetrafluoroethylene ethylene copolymer, can be illustrated.

[0016] Moreover, a macromolecule constituent which has alkali-metal ion conductivity, such as a lithium ion, especially can also be used as binding material. As a macromolecule which has such ion conductivity Polyether system high molecular compounds, such as polyethylene oxide and polypropylene oxide, A crosslinked polymer compound of a polyether, polyepichlorohydrin, poly FOSUFAZEN, A polysiloxane, a polyvinyl pyrrolidone, poly vinylidene carbonate, A system which compounded an alkali-metal salt which makes lithium salt or a lithium a subject with high molecular compounds, such as a polyacrylonitrile, Or a system which blended with this an organic compound which has high dielectric constants, such as propylene carbonate, ethylene carbonate, and gamma-butyrolactone, can be used. These materials may be combined and used.

[0017] A negative electrode for nonaqueous rechargeable batteries of this invention is produced by mixing metal particles and binding material and applying on a charge collector. A mixed rate of binding material to metal particles is 0.5 - 10 % of the weight more preferably 0.1 to 30% of the weight. By ****ing a mixed rate of binding material to 30 or less % of the weight, internal resistance of an electrode can be stopped within more desirable limits. Moreover, a moderate binding property can be given to a charge collector and metal particles by ****ing a mixed rate of binding material to 0.1% of the weight or more.

[0018] Especially a mixed method of metal particles and binding material is not restricted. According to a physical property of binding material, a solvent may be used at the time of mixing. A class and an amount of a solvent to be used can be suitably determined in consideration of viscosity of solubility and binding material to binding material, the dispersibility of metal particles, etc. Moreover, an additive other than metal particles and binding material may be mixed further. Mixture can be made into the shape of the shape for example, of a slurry, or a paste.

[0019] Mixture of metal particles and binding material is applied on a charge collector with a means well-known to this contractor. When mixture is a slurry-like, it can apply on a charge collector using a die coating machine, a doctor blade, etc. Moreover, when mixture is a paste-like, it can apply on a charge collector by roller coating etc. When a solvent is being used, a negative electrode can be produced by drying and removing a solvent.

[0020] Especially a configuration of a charge collector which applies mixture of metal particles and binding material is not restricted, but can be suitably determined according to a use mode of a negative electrode etc. For example, cylindrical, tabular, and a coiled form charge collector can be used. Even if the quality of the material of a charge collector is a metal and it is carbon, it is not cared about. It is desirable

to use metal thin films, such as a nickel foil, aluminium foil, and copper foil, as a charge collector especially in this invention. It is more desirable to use copper foil especially.

[0021] Especially a gestalt of metal particles made to adhere on a charge collector and binding material is not restricted, but can take various kinds of gestalten. For example, a gestalt which metal particles and a binding material particle mixed to homogeneity or an ununiformity, a gestalt to which fibrous binding material became entangled with metal particles, a gestalt to which a layer of binding material adhered on the surface of metal particles can be taken. Moreover, a charge collector to which metal particles were made to adhere in binding material can be fabricated in an electrode configuration of arbitration with roll forming, compression molding, etc. as it is. A configuration of an electrode is suitably determined according to a configuration of a nonaqueous rechargeable battery to manufacture etc.

[0022] Thus, it has an advantage that a produced electrode is high capacity occlusion and in being able to emit reversibly about alkali-metal ion, such as a lithium ion, and its fall of capacity by repeat of a charge-and-discharge cycle is also small. Moreover, according to an above-mentioned manufacture method which adds a reducing agent in a solution of a metal salt, it also has an advantage that it can mass-produce easily.

[0023] Especially a configuration and a process of a nonaqueous rechargeable battery using this electrode as a negative electrode can be suitably chosen from modes which are not limited but are usually adopted. A separator, a gasket, an obturation board, a cel case, etc. can be further used for a nonaqueous rechargeable battery if needed including a negative electrode, a positive electrode, and an electrolyte as a component at least. The process puts an electrode of this invention for example, on a cel floor plate, it can form the electrolytic solution and a separator on it, it can put a positive electrode so that it may counter with a negative electrode further, and it can use it as a rechargeable battery in total in a gasket and an obturation board. Especially a configuration of a rechargeable battery is not restricted but can be used as telescopic, a square shape, a coin mold, etc.

[0024] Especially a positive-electrode material used for a nonaqueous rechargeable battery of this invention is not restricted, but it can be used, choosing it suitably from positive-electrode materials of a rechargeable battery known from the former. concrete -- LiFeO₂, LiCoO₂, LiNiO₂, and LiMn₂O₄ and these non-stoichiometric compounds, MnO₂, TiS₂, FeS₂, Nb₃S₄, Mo₃S₄, CoS₂, and V -- 2O₅, P₂O₅, CrO₃, V₃O₃, TeO₂, and GeO₂ etc. -- it can use.

[0025] Since occlusion and an electrode which can be emitted are used for a nonaqueous rechargeable battery of this invention for alkali-metal ion or an atom as a negative electrode, a compound which has activity protons, such as water and alcohol, as the electrolytic solution cannot be used. For this reason, nonaqueous electrolyte or a solid electrolyte is used for a nonaqueous rechargeable battery of this invention. When using nonaqueous electrolyte, it is desirable to use an aprotic organic solvent with high electrical conductivity. For example, propylene carbonate, ethylene carbonate, diethyl carbonate, dimethyl carbonate, ethyl methyl carbonate, 1, 2-dimethoxyethane, gamma-butyrolactone, a tetrahydrofuran, 2-methyl tetrahydrofuran, a sulfolane, 1, 3-dioxolane, an ethylene sulfide, a dimethyl sulfide, dimethyl sulfoxide, an acetonitrile, etc. can be mentioned as a desirable solvent. A solvent used for nonaqueous electrolyte may be a kind, or may mix two or more sorts.

[0026] As for an electrolyte which constitutes nonaqueous electrolyte, it is desirable to choose from compounds which carry out ionic dissociation with a high degree of dissociation into a solvent to be used. as a concrete electrolyte -- LiClO₄, LiPF₆, LiBF₄, LiCF₃SO₃, LiAsF₆, LiSbF₆, LiCl, LiBr, Li(CF₃SO₂)₂N, LiC₄F₉SO₃, CF₃COOLi, and LiAlCl₃ etc. -- it can illustrate. An electrolyte may use only a kind independently and may use it beyond combining a NI kind. As for electrolytic concentration, it is desirable to make it about 0.5-2.0M.

[0027] Moreover, a solid electrolyte which is the conductor of alkali-metal ion, such as a lithium ion, can also be used for a nonaqueous rechargeable battery of this invention. for example, a solid polymer electrolyte and Li₂S-SiS₂, such as lithium perchlorate-polyethylene oxide, etc. -- an inorganic solid electrolyte etc. can be used.

[0028] It dissociates so that a positive electrode and a negative electrode may not contact physically, and a separator which constitutes a rechargeable battery of this invention has high ionic permeability, and it is desirable that electric resistance is low. A separator is chosen from stable materials to the electrolytic solution. Specifically, resin system porosity films, the above-mentioned gel solid electrolytes, etc., such as polyolefine system resin, can be used.

[0029] Thus, a nonaqueous rechargeable battery of manufactured this invention is high capacity, and even if it repeats charge and discharge, it has an advantage that there is little reduction in capacity. Moreover, since it can mass-produce by very simple method, availability on industry is also very high. It is useful if it is used for a field currently especially asked for small lightweight-ization, such as portable electronic communication equipment, such as a small video camera, a notebook computer, and a cellular phone, and a power supply of an electric vehicle. Moreover, a nonaqueous rechargeable battery of this invention can also be effectively used as a means of an energy storage. For example, it can use to storage of dump power, such as night and a weekend, and storage of energy intermittently produced like photovoltaics energy or wind-power-generation energy effectively.

[0030]

[Example] An example and the example of a comparison are given to below, and this invention is explained to it still more concretely. The material shown below, the amount used, a rate, actuation, etc. can be suitably changed, unless it deviates from the pneuma of this invention. Therefore, the range of this invention is not restricted to the example shown below. Moreover, although the following examples and examples of a comparison are estimating by producing a half cell, the same effect is expectable even if it uses the above-mentioned positive-electrode material as a positive electrode.

[0031] (Example 1) 7g of chlorination tin (II) dihydrates and 14g of sodium-citrate dihydrates were dissolved in 500ml of pure water at 3 degrees C among the ice bath. Apart from this, 2g of sodium hydroxides and 2.5g of sodium borohydrides were dissolved in 400ml of pure water in the ice bath. Both liquid was mixed in the ice bath, it stirred violently with the agitator for 3 hours, the solution presented gray, and the reaction was suspended in the place which the particle of a tin metal has generated. The obtained particle was filtered under nitrogen-gas-atmosphere mind, and pure water washed with 0.3-N hydrochloric acid after rinsing. Furthermore water and an acetone washed and the heating vacuum drying was carried out at 130 degrees C for 4 hours. The obtained fine particles were lightly cracked after radiationnal cooling, and the metal particles which prepared particle size to 300nm were obtained.

[0032] To 1g of these metal particles, N-methyl pyrrolidone solution of polyvinylidene fluoride (PVdF) was added 8% of the weight, and was agitated by solid content conversion, and the slurry was obtained. This slurry was applied on the stainless steel foil, and predrying was performed at 80 degrees C. After making it furthermore stuck by pressure, reduced pressure drying was carried out to discoid with a diameter of 20mm at punching and 110 degrees C, and it considered as the electrode. The separator made from polypropylene which carried out impregnation of the electrolytic solution to the obtained electrode was inserted, and the coin mold cel which the lithium metal

electrode was made to counter was produced. The solution made to dissolve lithium perchlorate in propylene carbonate by 1.0 mol/l was used for the electrolytic solution.

[0033] The charge and discharge test was performed using three coin mold cells manufactured by this method. A charge and discharge test is current density 0.3 mA/cm². It dopes until the potential difference between poles is set to 0V, and it is 2 the current density of 0.3mA/cm. It carried out by repeating the dedoped cycle until the potential difference between poles of Li and an active material was set to 1.5V. The first time, the 5th time, and the 10th dedope capacity were measured, and it asked for the cycle capacity recovery factor expressed with the following formulas. A result is shown in a table 1.

[0034]

[Equation 1]

$$\text{サイクル容量回復率 (\%)} = \frac{(\text{第n回目の脱ドープ容量})}{(\text{初回の脱ドープ容量})} \times 100$$

n= -- 5 and 10 [0035] (Example 2) Antimony chloride (III) 1.6g, 5g of chlorination tin (II) dihydrates, and 19g of citric-acid NATORIUMUNI hydrates were dissolved in 500ml of pure water at 3 degrees C among the ice bath. Apart from this, 2g of sodium hydroxides and 2g of sodium borohydrides were dissolved in the ice bath the same [250ml of pure water]. Both liquid was mixed under ice-cooling and the same actuation as an example 1 was performed after that. As a result of performing an X diffraction to the obtained metal particles, it was checked that these metal particles are Sn-Sb compound alloys. Particle size was 300nm. The result of having measured the 5th time and the 10th cycle capacity recovery factor by the method indicated by the example 1 is shown in a table 1.

[0036] (Example 1 of a comparison) Instead of the metal particles in an example 1, the commercial tin metal (particle size of 35 micrometers: Aldrich make) was used as it was, without giving acid cleaning. The other actuation was performed like the example 1. The result of having measured the 5th time and the 10th cycle capacity recovery factor by the method indicated by the example 1 is shown in a table 1.

[0037]

[A table 1]

	実施例 1	実施例 2	比較例 1
第5回容量回復率	90%	89%	76%
第10回容量回復率	43%	93%	0%

[0038]

[Effect of the Invention] The manifestation of the capacity exceeding the geometric capacity of a graphite is possible for the rechargeable battery of this invention, and over a long period of time, it is efficient and can perform occlusion of alkali-metal ion or an alkali-metal atom, and emission. Moreover, the nonaqueous rechargeable battery of this invention can be manufactured in large quantities by the simple method, and fits industrial production. Therefore, according to this invention, the lithium ion battery of high capacity etc. can be offered in large quantities.

[Translation done.]